

By considering actual timings (IST) of individual spells of either polarity, time occupied during each hour interval (1300–1400, 1400–1500, etc) was found and expressed as percentage of the seasonal total time (Table 4). It is noticed that 72 to 87% of the total duration of point discharge current was limited up to 2000 h during both seasons. However on looking for the activity beyond mid-night hours (2300–2400) we notice that during 1987, 19% of time for negative current and 6% of time for positive current was occupied and the activity lasted until early morning hours. Such a feature was not noticed during 1988 season. The extreme edge of diurnal activity of point discharge current in 1988 was up to 0000–0100 h.

The above results suggest that thunderstorms in May–June contributed for excess positive charge than negative charge, and thunderstorms in April contributed for excess negative charge. In 1987 longer durations of positive current prevailed than those of negative and in 1988 the reverse was noticed. During 1987 an appreciable duration of point discharge current persisted even beyond mid-night hours unlike in the year 1988. However, since the above results are based on limited observations these inferences should be taken with sufficient reservation and detailed verification is necessary from future works.

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Study of rapid reactions by the steady state principle: kinetics of the reaction between vitamin C and iodine in aqueous solution

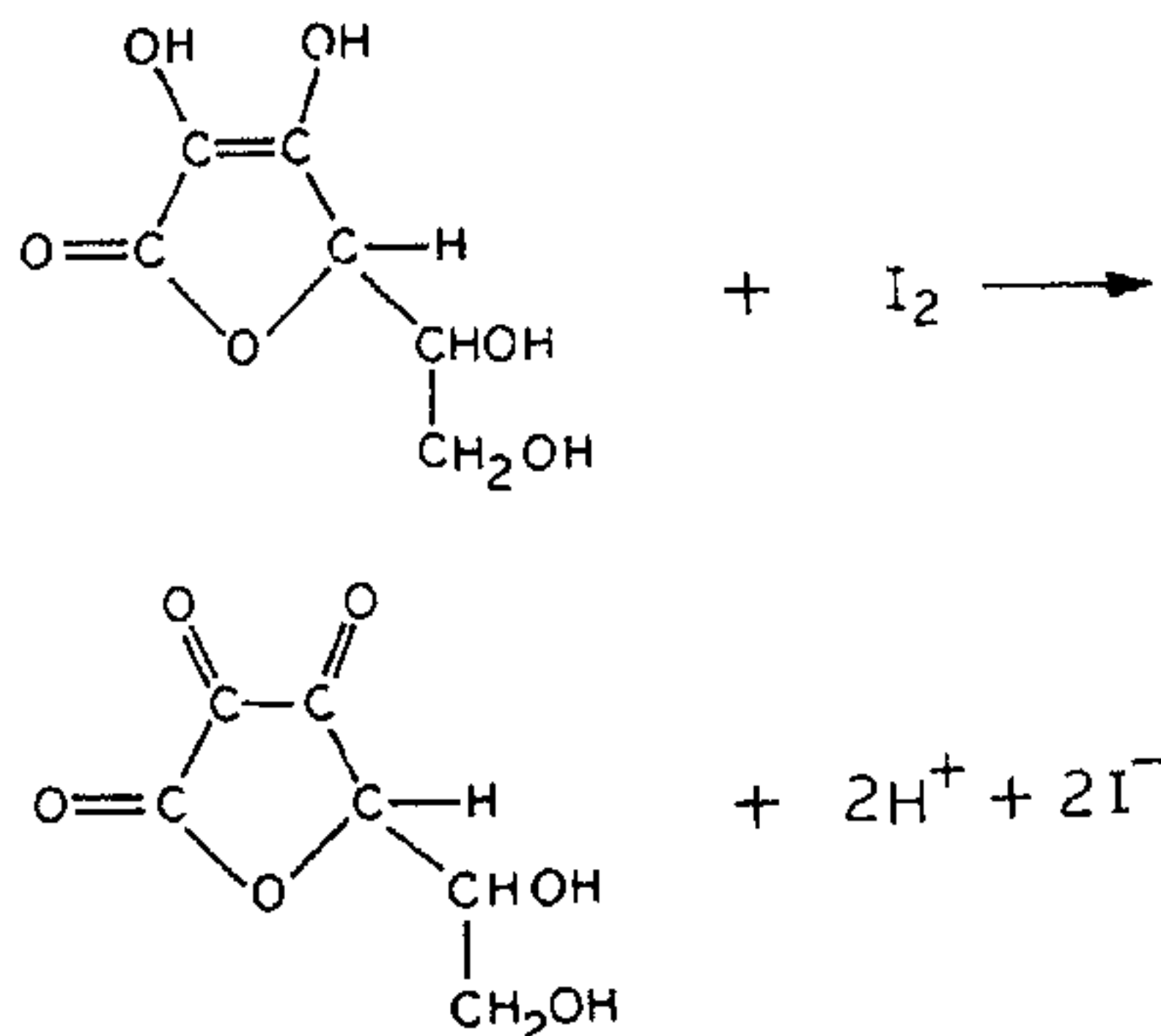
T. S. Rao, M. M. Murhe, R. B. Dabke and T. Harikrishna

Department of Chemistry, University of Poona, Pune 411 007, India

The kinetics of the rapid reaction between vitamin C and iodine has been studied by the steady state principle in which iodine is produced at a known rate by the persulphate–iodide reaction and is simultaneously consumed by vitamin C. The effective concentration of iodine during the steady state, which is very low, is measured from its redox potential at a platinum electrode. Vitamin C reacts rapidly with iodine and at 25°C the specific reaction rate is $8.18 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. The frequency factor is $1.82 \times 10^{15} \text{ M}^{-1} \text{ s}^{-1}$, the energy of activation is 53.1 kJ mol^{-1} and the entropy of activation is $-37.7 \text{ J mol}^{-1} \text{ deg}^{-1}$.

VITAMIN C (L-ascorbic acid) has been known since long as an effective reducing agent which has found broad applications in polarographic analysis^{1–3} and medicinal chemistry^{4,5}. It is an ene-diol γ -lactone in which the strong reducing property depends upon the loss of hydrogen atoms from the hydroxyls on the ene-diol carbons.

Vitamin C reacts quantitatively with iodine according to the equation

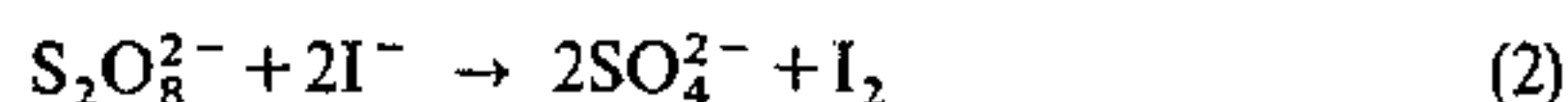


In this work iodine is present mostly as the tri-iodide ion, I_3^- , but for simplicity it is represented as I_2 .

The reaction occurs rapidly and, surprisingly, the kinetics of the reaction has not been reported in the literature. The usual spectrophotometric technique for the study of rapid reactions is of limited use in the present case because at low concentrations of the reactants needed for such technique, the absorption due to iodine is too low for accurate measurements. Hence

in the present work the kinetics of the reaction has been studied by the steady state principle.

In this technique instead of mixing vitamin C and iodine and then trying to follow the course of the reaction, the iodine is produced *in situ* at a controlled rate by the well-known persulphate-iodide reaction⁶⁻⁸ and is simultaneously consumed by vitamin C, leading to a steady state. In the reaction



the rate of production of iodine can be determined from the specific reaction rate and the concentrations of the reactants. Now, if, in this system, a low concentration of vitamin C is present, since it reacts rapidly with iodine, a steady state is attained wherein the rate of production of iodine

$$\frac{d[\text{I}_2]}{dt} = k_2 [\text{S}_2\text{O}_8^{2-}] [\text{I}^-] \quad (3)$$

and its rate of consumption

$$-\frac{d[\text{I}_2]}{dt} = k [\text{I}_2]_* [\text{C}_6\text{H}_8\text{O}_6] \quad (4)$$

are balanced. The effective concentration of iodine $[\text{I}_2]_*$ at the steady state, which is very low, is estimated from its redox potential. It is then possible to determine the specific reaction rate of the vitamin C and iodine reaction as explained later.

This technique presumes that the vitamin C reacts only with iodine and not directly with persulphate. In separate experiments it had been observed that the concentration of vitamin C remained significantly the same even in the presence of persulphate as shown by its polarographic oxidation wave.

Analytical reagent grade chemicals (BDH/E. Merck/Sarabhai) and double distilled water were used to prepare all the solutions. The following stock solutions were prepared: A, 0.040 M $\text{K}_2\text{S}_2\text{O}_8$; B, 0.16 M KI; C, 0.002 M $\text{C}_6\text{H}_8\text{O}_6$.

Twenty ml of A and 10 ml each of B and of C were pipetted out into separate beakers and placed in thermostat at 25°C. A bright platinum foil electrode (1 cm²) and a SCE were placed in B. To this 20 ml of A was added, a stop-watch was started simultaneously and then 10 ml of C was added. The EMF was measured with an AGRONIC-DPM electronic voltmeter after stirring the mixture and at intervals of 10 sec for about 3 min. The EMF was plotted versus time and the linear curve was extrapolated to zero time. This is advantageous because at zero time the concentrations of various reactants are known accurately. From this, one could obtain the effective concentration of iodine at that instant.

The effective concentration of iodine at zero time was evaluated from a calibration curve obtained as follows. Several iodine solutions in the concentration range

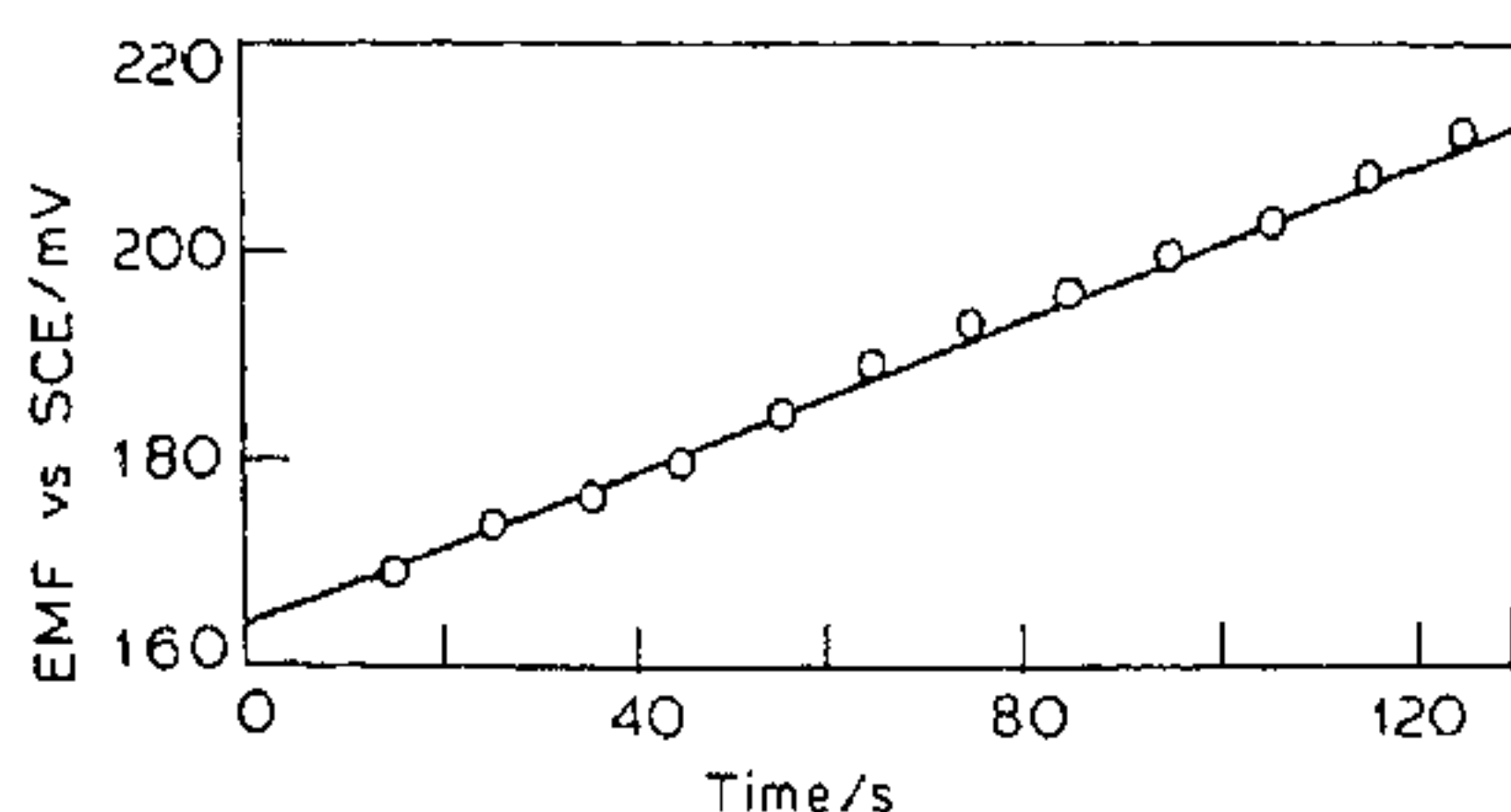


Figure 1. Redox potentials of iodine/iodide system under steady state condition. Temperature = 25°C.

from 10^{-4} M to 10^{-7} M were prepared in solutions containing 0.040 M KI and 0.020 M K_2SO_4 . The latter provided the same ionic strength as $\text{K}_2\text{S}_2\text{O}_8$ in the actual reaction mixture. The redox potentials of these solutions were measured using the same platinum electrode and SCE. Based on Nernst equation the redox potentials were plotted versus $\log [\text{I}_2]$ and as expected a straight line was obtained. From this calibration plot one could evaluate the effective concentration of iodine at the steady state from the measured redox potential. From these results the specific reaction rate was determined, as explained later.

Similar studies were carried out at various temperatures in the range 15°C to 40°C for steady state measurements, rate of production of iodine and calibration. From these results the activation parameters of the reaction were evaluated.

The specific reaction rate for reaction (2) determined by the conventional way was found to be $3.22 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. Hence the rate of production of iodine, from equation (3) was $3.22 \times 10^{-3} \times 0.02 \times 0.04 = 2.58 \times 10^{-6} \text{ M s}^{-1}$ since the concentrations of persulphate and iodide were 0.02 M and 0.04 M respectively. The redox potential due to effective concentration of iodine at the steady state $[\text{I}_2]_*$ obtained by extrapolation of EMF versus time (Figure 1) was observed to be 165 mV. Hence from the calibration curve (Figure 2) the effective

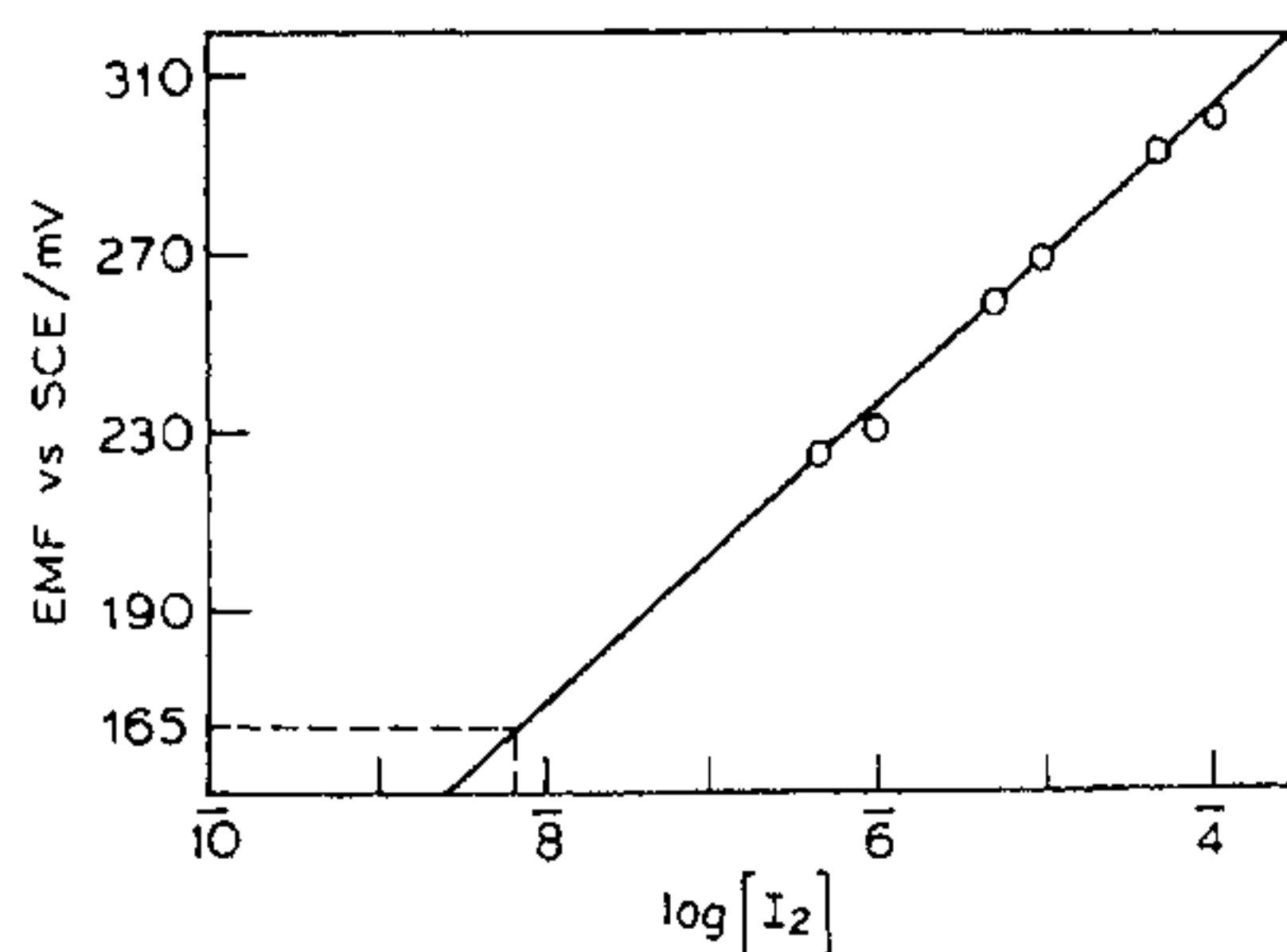


Figure 2. Redox potentials of iodine/iodide system at various concentrations of iodine. Temperature = 25°C.

concentration of iodine was 6.31×10^{-9} M. Since at the steady state the rates of production and consumption of iodine are balanced,

$$k_2 [S_2O_8^{2-}] [I^-] = k [I_2]_* [C_6H_8O_6]. \quad (5)$$

The left hand side of the equation has been shown to be $2.58 \times 10^{-6} \text{ M s}^{-1}$. Substituting for this in equation (5)

$$2.58 \times 10^{-6} \text{ M s}^{-1} = k \times 6.31 \times 10^{-9} \text{ M} \times 5 \times 10^{-4} \text{ M}$$

where 5×10^{-4} M was the concentration of vitamin C in the reaction system. Hence

$$k = \frac{2.58 \times 10^{-6}}{6.31 \times 10^{-9} \times 5 \times 10^{-4}} \\ = 8.18 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}.$$

From the results of similar measurements at various temperatures and from the Arrhenius plot, the energy of activation for the reaction was evaluated to be 53.1 kJ mol^{-1} . The frequency factor at 25°C was $1.82 \times 10^{15} \text{ M}^{-1} \text{ s}^{-1}$ and the entropy of activation was $-37.7 \text{ J mol}^{-1} \text{ deg}^{-1}$.

Limits of error. It is evident in this technique that the accuracy of determination of the specific reaction rate, k , depends much upon the accurate determination of the effective concentration of iodine at the steady state evaluated from its redox potential. The other factors affecting the specific reaction rate can be controlled with greater precision. Since the redox potential due to iodine at the steady state is reproducible to ± 1 mV, the error in the determination of the effective concentration of iodine at the steady state is about $\pm 6\%$ and hence k values have an error of this magnitude.

It may be mentioned that although $S_2O_8^{2-}/SO_4^{2-}$ has a redox potential greater than that of I_2/I^- , yet, the former does not give rise to a reversible electrode⁹ and therefore it is only the redox potential due to I_2/I^- which is being measured at the steady state.

In the present work the objective was to determine the specific reaction rate of a rapid reaction by applying the steady state principle and no particular efforts have been made to investigate the mechanism of the reaction.

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Forms and distribution of potassium element in salt-affected aridisol

P. K. Laghate*, S. C. Gupta* and D. D. Dubey

Salt Affected Soils Project, JNKVV Campus, College of Agriculture, Indore 452 001, India

*Present address: R.A.K. College of Agriculture, JNKVV Campus, Sehore 466 001, India

Two typical salt-affected soils were investigated for different forms of potassium. The available K was only 0.8–3.4% of the total soil K. The Gibb's free bonding energy indicated strong preference of K to Na in the K–Na system. The surface layer showed preference to K while the lower layers showed preference to Ca in the K–Ca system. The relative stability diagram showed that K-feldspar is the stable phase followed by mica. The sand contributed highest K to the soil followed by silt and clay. The mica increased while K-feldspars decreased with the decrease in particle size. The fluctuating water table also played a vital role in the K distribution in the soil.

POTASSIUM is found in most of the soils in varying amount depending on the weathering conditions and stage of soil formation¹. The forms and distribution of potassium and content of potassium-bearing minerals of salt-affected soils may provide the much-needed information about the degree and stage of weathering, soil formation, potassium supplying power of soil and their management. The present study was, therefore, made to assess different forms of potassium in soil and soil fractions of typical salt-affected soils of Banaskantha district, Gujarat.

Two typical salt-affected pedons belonging to Typic Natrargids (Taluka Deodar) and Aquic Natrargids (Taluka Santalpur) were exposed for collection of horizon samples. The morphology, particle size distribution and particle fractionation have been reported elsewhere². The water soluble and exchangeable K were determined by the procedure outlined by Richards³; the fixed K and total K in soil and soil separates by the methods of Jackson⁴, and the lattice K from the difference between the total K and the sum of water soluble exchangeable and fixed K. The feldspars K and mica K in soil separates were determined after sodium pyrosulphate fusion⁵. The mean free bonding energy between K and Na was calculated according to Marshall⁶.

The data in respect of forms of K, content of K in soil fractions and Gibbs free energy of exchange